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GRAPHITE FIBER OXIDATION

By
John C. Goan

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UNITED STATES NAVAL ORDNANCE LABORATORY, WHITE OAK, MARYLAND

ATTENTION

34

GRAPHITE FIBER OXIDATION

Prepared by:
John C. Goan

ABSTRACT: In order to improve the low interlaminar shear strengths which hinder widespread use of epoxy composites made from high modulus graphite fibers, an investigation was made of fiber surface treatments. Treatment of the fibers with various oxidizing systems was found to increase composite interlaminar shear strengths as much as twofold. Among the oxidizing agents studied, concentrated nitric acid was the most effective in increasing fiber-resin adhesion without significantly decreasing fiber strength. Exposure of the fiber to low pressure oxygen in the presence of an R. F. plasma was also an effective treatment.

The mechanism by which fiber oxidation improves composite shear strength appears to be related both to an increase in fiber surface area and to an alteration of the nature of the surface resulting from the attachment of oxygen-containing functional groups.

APPROVED BY:

F. Robert Barnet, Chief
Non-Metallic Materials Division
CHEMISTRY RESEARCH DEPARTMENT
U. S. NAVAL ORDNANCE LABORATORY
WHITE OAK, SILVER SPRING, MARYLAND

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GRAPHITE FIBER OXIDATION

This report contains the promising results of a project aimed at improving the
fiber-to-resin bonding in graphite fiber reinforced plastics, which are among
the most attractive of the high performance composite materials. The work is
of an experimental nature and involves only one possible approach to the problem.

This project has been funded by the Naval Air Systems Command under Task A32 520/
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and December, 1968.

                              GEORGE C. BALL
                              Captain, USN
                              Commander

                              ALBERT LIGHTBODY
                              By direction

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INTRODUCTION

The search for strong, lightweight materials of construction has, in recent years, received the attention of an increasing number of materials specialists. One of the most promising results of their work has been the family of graphite fiber reinforced plastics. The properties of these materials have been advancing at a remarkable rate. As an index of this growth, consider that in 1967 the best commercially marketed graphite fiber available from one vendor possessed a nominal tensile modulus of 25 million psi. Now this same manufacturer has made available yarn with a nominal tensile modulus of 75 million psi. Conservative forecasts indicate that materials with 80 to 90 million psi modulus will soon be available.[1] Fiber strengths of over 400,000 psi have been measured; this value is not considered to be the limit. Even in comparison with other high modulus fibers, such as boron, the use of graphite for plastic reinforcement has a very bright future.

In spite of the promise graphite fibers hold for making reinforced plastics and other composites with uniquely high strengths and stiffnesses, there do remain significant problem areas. One of these is the low interlaminar shear strength. Typical values for shear strengths of unidirectional epoxy composites made from untreated graphite fibers are given in Table I, which also includes data from S glass and boron composites. Values for most of the graphite fiber composites are unacceptably low when compared to the other fibrous reinforcements listed.

A further distressing trend is evident on examining the data in Table I, namely that composites made from the low modulus graphite fibers have adequate shear strength, but those made from the more attractive high modulus materials do not. Clearly, this is an undesirable situation.

The need to improve the shear strength in graphite fiber composites has been recognized for some time, and there have been several attacks on the problem.[1] The basis for most attempts has been to modify the fiber surface in such a way as to improve the adhesion between the fiber and the resin. No doubt, this approach has been taken because it had been successful in overcoming interlaminar shear strength problems in glass fiber composites.

One fiber treatment resulting in very dramatic increases in graphite composite shear strength is called "whiskerizing." This involves the growth of silicon carbide whiskers directly on the fiber surface from reactants in the vapor phase.[1,2,3,4,5] This process, developed under contract for the Naval Ordnance Laboratory, has given composites with shear strengths well in excess of 12,000 psi. A unique feature of this treatment process is that the whisker growth on the fiber lends to the composite a three-dimensional character that results in increased transverse properties.

A different type of surface treatment process has been the object of study by other workers. This second approach, which involves the activation of the fiber surface by a variety of chemical attacks, has also met with a degree of success. Herrick[6,7,8], Novak[9], and Steingiser[10] are among the investigators who have found that the interlaminar shear strength of graphite composites can be

increased up to twofold by exposure of the fiber to the proper oxidizing conditions. The British Morganite and Courtalds fibers have been given very effective surface treatments. Though no details about the processes have yet been released, they appear to be some sort of oxidative treatment. Thus, fiber oxidation also has great promise in increasing composite shear strength and other properties that derive from the fiber-to-resin bonding.

Evaluation of the type of surface treatment based on oxidation has been the object of the work included in this report. Offering great advantages in simplicity and applicability to continuous processing, surface oxidation has been a particularly attractive candidate as a fiber treatment to improve the interlaminar shear properties of graphite fiber composites.

A further goal of the program has been to develop information on the surface chemistry and morphology of graphite fibers and, subsequently, to determine how these properties are affected by oxidation of the fiber. Though the area of the fiber surface and the nature of the chemical groups present obviously exert a profound effect on the fiber-resin adhesion, comparatively little was known about the fiber surface pertaining to these properties. Very recently, however, reports have begun to appear which contain the results of fiber surface studies.[1,11,12]

It will be evident on reading this report that a basic philosophy of study has been followed in the program. This approach is the following: The effect of a given treatment process on a graphite fiber can realistically be determined only by incorporating the treated fiber into a resin composite and measuring the properties of the composite. As justification for this type of study, it is evident that many of the usual physical and chemical techniques of analysis are not capable of detecting the small differences in graphite fiber surfaces which can result in large differences in composite properties. Thus, evaluating graphite fiber treatments by means of evaluating the resulting composite has been not only practical but necessary. This is not to say that other analytical techniques are of no use -- indeed, they are, as this report will show -- but it is clear that the most meaningful tool presently available for evaluating fiber-resin adhesion is the fiber-resin composite. This is still the situation in glass reinforced plastics as well, in spite of the great strides made recently in surface chemistry and micromechanics.

MATERIALS

Most of the work in this report was done on the Thornel graphite fibers, manufactured by the Union Carbide Corporation, Cleveland, Ohio. These materials, made by the carbonization and graphitization of a rayon precursor, are available in continuous form. In the beginning, only the 25 million psi modulus Thornel 25 was available; it was later supplanted by Thornel 40 and Thornel 50 (the numbers refer to the nominal fiber modulus in millions of pounds per square inch).

The Thornel fibers are normally supplied with a polyvinyl alcohol (PVA) sizing in order to improve the handling properties of the yarn. Since the PVA coating tends to obscure the true nature of the graphite fiber surface, yarn without the PVA sizing was obtained for the surface treatment studies. Thornel 50 yarn, however, was not conveniently available without the PVA coating, and the normal commercial material was therefore studied.

Figures la and lb are high resolution scanning electron photomicrographs of Thornel 40 graphite fiber surfaces. The fiber is in the form of a yarn bundle made from two twisted strands, each containing 720 individual filaments. The average filament diameter is about 7 microns. Note in Figure la the striations parallel to the fiber axis which are typical of the high modulus fibers. Note also in Figure lb the broken end of the filament and the hole appearing in the segment broken off. These holes are commonly observed; they apparently result from the pyrolysis process and account for the less than theoretical density of the fiber.

Treatments of the British RAE and Morganite fibers were also studied. These materials, made from a polyacrylonitrile precursor, were initially available in short lengths of tow, and only the short lengths could be treated. Fibers are now available in continuous form from the United Kingdom manufacturers, Morganite and from Courtalds, Ltd., and their American affiliates. Like the Thornel fibers, the British fibers have an average filament diameter of about 7 microns.

The resin used for making composites from the surface-treated fibers was Union Carbide's ERL-2256. It has the following approximate composition:

Liquid diglycidyl ether bisphenol A resin - 62.5%

Bis(2,3-epoxycyclopentyl)ether (liquid isomer) - 37.5%

The curing agent, used at the nominally stoichiometric concentration of 27 phr, was Union Carbide's ZZL-0820, a eutectic mixture of metaphenylene diamine and methylene dianiline.

EXPERIMENTAL

SOLUTION OXIDATIONS

The most intensively studied chemical treatment of graphite fibers was activation of the surface by various wet oxidizing systems, of which the principal one as 60% aqueous nitric acid. About 10 grams of yarn (enough to wind an NOL ring) were wound on an open glass spool (Figure 2), washed with distilled water and dried to constant weight by heating to 150°C in vacuum. Yarn which was not continuous was cut into 8-inch lengths and placed in a glass tube open at both ends but with small enough diameter to keep the strands oriented in the same direction. The spools were immersed completely in the nitric acid in a resin flask fitted with a thermometer, reflux condenser, and heating mantle. The system was brought rapidly to boil (120°C for 60% nitric acid) and kept at reflux for various treatment times ranging up to 48 hours. After treatment, all traces of acid were removed by washing the yarn for several hours in flowing tap water followed by boiling with two changes of distilled water. The spool was again dried to constant weight in vacuum.

Other solution oxidation treatments were conducted in essentially the same way. Variations involved the concentration of reagents, the treatment temperatures and times. Sodium hypochlorite oxidations were made with a 5.5% solution equivalent to undiluted commercial bleach.

GASEOUS OXIDATIONS

For air oxidation ten grams of yarn were wound on a stainless steel spool and heated in an oven at 400°C ±10°C for periods of 16 to 30 hours. The yarn was weighed before and after treatment to determine weight loss.

Ozone oxidation was accomplished by placing the glass spool containing the yarn (Fig. 2) in a resistance heated glass tube constructed to allow a current of gas through the tube. The gas mixture consisted of 50% oxygen, 45% Freon 13, and 5% ozone (Matheson Gas Co.). This was passed at the rate of 100 cc/min through the tube which was heated to 100°C. Three hours was the usual treatment time.

Some preliminary work has been done on continuous gas phase oxidations, using the apparatus shown in Figure 3, which was originally developed for chemical vapor deposition treatments of the fiber. In this apparatus the fiber was heated by its own electrical resistance as it was drawn across two graphite pulleys connected to an alternating current source. The temperature was monitored by optical pyrometry. The heated yarn was exposed, while passing through the tube, to various oxidizing atmospheres; air being the most studied example. Oxidation studies using the continuous treater are in an early stage of development.

RADIO FREQUENCY PLASMA OXIDATION

Exposure of the graphite yarn to oxygen at reduced pressure in the presence of an electrodeless RF discharge was used to activate the fiber surface. Electrical energy was coupled inductively into a low pressure oxygen stream which was allowed to flow over a spool of yarn in the reaction chamber. No external heating of the chamber was employed. Figure 4 is a schematic drawing of the apparatus, which is not a commercial unit but was constructed at NOL. Figure 5 is a photograph of the yarn in the presence of an oxygen plasma. Conditions for a typical oxidation experiment were as follows:

R. F. Frequency: 100 Megahertz

Discharge Potential: 330 Volts

Discharge Current: 170 Milliamps

Reaction Time: 3 Hours

Oxygen Pressure: 0.15 Torr

Assuming a coupling efficiency of 75%, the power level developed in the oxygen plasma was about 43 watts. This produced a glow in the chamber which was initially lavender but changed to blue as the oxidation reaction proceeded and the carbon dioxide concentration in the gas increased.

FABRICATION OF COMPOSITES

Most of the treatment work was carried out on continuous Union Carbide Thornel Fibers. With these it was possible to wind NOL rings in accord with ASTM 2291-65T. Standard 6-inch rings required about 10 grams of yarn. In order to be able to evaluate smaller amounts of treated yarn, some 3-inch rings,

containing about three grams of yarn, were fabricated by the same method. In general, the yarn was vacuum impregnated with the resin prior to winding. Because of the low breaking strength of most of the yarns, the tension on the strands during winding was kept below 10 ounces. Even at this low strand tension, the resin content in the composites was maintained below 45 weight percent.

Fibers available only in short lengths or too weak to wind into NOL rings were molded into straight bars. The procedure for making these bars has been described.[3]

MECHANICAL TESTS

Composite interlaminar shear strength was measured on NOL ring segments in accord with the short beam test, ASTM-2344-65T. The usual span-to-depth ratio was five to one. Segments of the 3-inch NOL rings were tested at 6:1 span-to-depth ratio; the straight bars were measured at 5:1.

There has been up to now a considerable variation in the techniques for measuring the tensile strength of graphite fibers. In early work, ASTM D2343-65T, developed for testing glass yarn, was used as the test method. The long gauge length specified in this method led to a very high coefficient of variation, presumably because of the lack of uniformity of the strands. Furthermore, the strands usually broke at the grips. More recent practice has been to use 2-inch or shorter gauge lengths and a different tab (grip) arrangement. A current round-robin test in progress under the auspices of ASTM will hopefully result in a satisfactory method for measuring the tensile strength of graphite fibers. What can be said concerning the tensile strength data in this report is that the data for a given fiber, e.g. Thornel 25, and its treated derivatives were obtained by the same method. The data on the effect of a surface treatment process on the tensile strength of a given fiber are therefore reliable. However, because of the differences in test methods, the data for different fibers are not comparable.

SURFACE AREA MEASUREMENTS

Fiber surface areas were determined from the nitrogen adsorption isotherms at 77°K. A standard volumetric apparatus was used for the measurements.[13] Five-gram samples were degassed for three hours at a temperature of 200°C and a vacuum of 0.01 Torr before measurement. Figure 6 shows a typical adsorption isotherm. Surface areas were obtained from the isotherm data using the Brunauer, Emmett and Teller (BET) equation.[14] To simplify the otherwise tedious calculations, computations were made in a digital computer using the BASIC programming language. Figure 7 is the BET plot derived from the adsorption isotherm data given in Figure 6.

CHEMICAL ANALYSIS

Analysis for oxygen-containing functional groups on fiber surfaces was carried out by Schwartzkof Microanalytical Laboratories in New York, using the procedures of Rivin,[15] Boehm,[16] and de Bruin.[17] Carboxyl (-COOH) content was determined by suspending the fiber in a calcium acetate solution and measuring the acetic acid liberated by the ion exchange reaction. Total active hydrogen content was obtained by reacting the fiber with an ether solution of lithium aluminum hydride and measuring volumetrically the hydrogen gas evolved.

The difference between the total active hydrogen and that due to carboxyl was taken to be phenolic hydroxyl. The total oxygen content was determined by standard difference methods.

RESULTS

EFFECT OF FIBER OXIDATION ON COMPOSITE SHEAR STRENGTH

The interlaminar shear strength of Thornel 25 epoxy composites was increased by various fiber oxidation treatments, as is seen in Figure 8. Oxidation with nitric acid had the greatest effect (80%) on shear strength, while at the same time it had the least deleterious effect (2%) on strand tensile strength (Table II). Other oxidative processes also increased composite shear strength but to a somewhat lesser extent than the nitric acid treatment. Many of the treatments severely decreased the tensile strength of the fiber (as much as 27%). The rather small increase in composite shear strength resulting from treating the yarn with ozone was surprising in view of the reported rapid attack of ozone on graphite.

Treatment of the yarn in the low pressure radio frequency oxygen plasma was equivalent to air oxidation in its effect on composite shear strength but was less damaging to the fiber, as shown by the comparative decreases in fiber tensile strength.

The data for Thornel 40 composites is given in Figure 9. These appeared to be even more responsive than the Thornel 25 composites to fiber oxidation, since shear strengths in excess of 8000 psi were measured on NOL rings made from Thornel 40 yarn treated with nitric acid. Air oxidation and oxidation in the RF plasma gave about the same shear strength results, but the RF oxidation process gave a measured tensile strength higher than that resulting from air oxidation (Table II).

The results accumulated to date on Thornel 50 composites, given in Table III, indicate that oxidation of Thornel 50 had less effect on composite shear strength. No shear strength values greater than 6000 psi were obtained by any fiber oxidation treatment. The low values may be a result of the drastic decrease in fiber tensile strength in oxidized fiber. It was often found that the failure mode in the short beam test was not interlaminar shear but was instead a tensile break. When this occurred, a true value of interlaminar shear strength was not obtained; the actual shear strength may very well be higher than given in Table III.

A few other fibers were oxidized with nitric acid to determine the effect on composite shear strength. The results on these materials are given in Table IV. Two points are of interest in this data. First, the HITCO HMG 25 was severely weakened by the treatment and the shear strength figure given does not represent the true shear strength, since a tensile failure occurred. Second and more important was the very high shear strength obtained by treating Morganite I fiber. To our knowledge, the value of 9600 psi is the highest shear strength reported for any Morganite I epoxy composite. The proprietary British surface treatment, which is also an oxidation process, ordinarily gives Type I composites with about 8000 psi interlaminar shear strength.

Boiling water conditioning of composites made from surface oxidized fibers had no appreciable effect on the interlaminar shear strength. Data for Thornel 25 composites is presented in Table V; tests on Thornel 40 and other oxidized fibers gave essentially the same results. Simon and Prosen[18] have previously reported that water exposure lowers the strength of carbon fiber composites only in cases where the fiber is either porous or has a water-soluble polyvinyl alcohol coating. A 72-hour water boil test on a composite made with nitric acid treated Thornel 40 resulted in a 3% increase in shear strength.

CHEMICAL FINISHES

Coating of both oxidized and unoxidized graphite fibers with polymers and reactive monomers was undertaken. The principle was that carboxyl and phenolic groups on the surface of oxidized graphite should be able to react with, for example, the isocyanate groups in a urethane prepolymer. Other isocyanate groups in the coating would be available to couple with the resin. The polyisocyanates would thus act as bridging or coupling agents between the polymer and the resin. When, however, composites were made from fibers treated in this way, they exhibited no significant improvements over composites made from fibers which had been oxidized but not treated with a coupling agent.

Other polymer coatings, for example nylon, .. had no appreciable effect on shear strengths of composites. One glass finish, A-1100, gamma-aminopropyltriethoxy-silane, when applied to an oxidized Thornel 25 surface, resulted in a composite with a shear strength slightly higher than composites made with oxidized fibers without coupling agents. It is possible that the phenolic hydroxyl groups on the oxidized fiber surface react with the finish in a similar fashion to the silanol groups on the surface of glass.

CONTINUOUS OXIDATION

The apparatus shown in Figure 3 was used for the continuous oxidation in air of Thornel 40 yarn. Exposing the fiber for 30 seconds to a temperature of 700°C and immediately thereafter passing the fiber through a dilute solution of epoxy resin to prevent fiber recontamination was somewhat effective in increasing composite shear strength but at great cost to the fiber tensile properties. Continuous fiber oxidation methods will receive further attention.

DISCUSSION

The results of using fiber oxidation to improve the shear strengths of graphite fiber-epoxy composites have confirmed the findings of Herrick and Novak.[5,9] Depending on the type of graphite fiber, a composite interlaminar shear strength increase of up to threefold can be obtained by the proper oxidizing treatment. In fact, the proprietary British surface treatment, presumably an oxidation process, has resulted in graphite composites with shear strengths in excess of 13,000 psi.

The reasons why fiber surface oxidation affects the shear strength of composites are probably complex. Goan and Prosen[1] have discussed the graphite fiber surface and pointed out some of the parameters important to adhesive bonding. Among the most important of these properties are the surface area and the nature of the surface. Either or both of these may be significantly altered by a surface oxidation.

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We know, first of all, that oxidation takes away some of the fiber. The weight loss data, given in Table VI, show that no more than one or two percent of the fiber is lost on oxidation; this, therefore, indicates that deep attack on the fiber has not occurred and that primarily the surface has been altered.

It is reasonable to expect a surface weight loss to be reflected in some change in the fiber surface area. The figures on the BET surface area measured by nitrogen adsorption are given in Table VII. These numbers demonstrate that surface area did increase with fiber oxidation, but only in the case of the nitric acid treated material was there a significant change. Such an increase in surface area would tend to improve the mechanical bond between the resin and the fiber. It is, however, noticeable that treatment processes, such as air oxidation or RF plasma oxidation, both of which raise fiber surface area about 60%, give composites with a comparable (50%) increase in shear strength, whereas the nitric acid treatment, which raises fiber surface area by about tenfold, gives only a twofold increase in composite shear strength.

Evidently, surface area increase is not the only reason why fiber oxidation improves composite shear strength. It is possible, of course, that shear strength is proportional to surface area only up to some value and then levels off.

Furthermore, as Quackenbush[19] has shown, the average pore diameter in carbon fibers is only about 7 $\mathring{A}$. This is too small for resin molecules to enter. Though such pores would greatly affect the total surface area and volume as measured by nitrogen adsorption, these small pores would not contribute much to the mechanical bond between the fiber and the resin. The shape of the adsorption isotherm curve for the nitric acid treated fiber in Figure 6 is typical for a Type IV isotherm, which is found when small pores are present.[20]

In this connection, Novak[9] has presented evidence from electron photomicrographs that air oxidation at 475°C heavily pitted the surface of Thornel 25 filaments. Novak reported no correlating surface area measurements. Didchenko[11] has also studied the effect of fiber oxidation on the surface morphology. He found that gentle chromic acid oxidation did not significantly increase the total BET surface area or pore volume, but it did shift the pore profile in the direction of forming a greater number of comparatively large (400 $\mathring{A}$) pores. These large pores would be relatively more accessible to the resin than the small pores present in the untreated fiber.

In summary, the work here and that reported elsewhere tend to indicate that surface area increase is probably not the primary reason why fiber oxidation improves the shear strength of graphite fiber-epoxy composites.

An alternative possibility is that fiber oxidation changes the nature of the surface and thereby alters the bonding properties. It should be remembered that adhesive bonds are affected as much by the type of bonding surface as by the interfacial areas.

It is well known that oxygen is readily chemisorbed on graphite, and that a pure carbon surface is not commonly observed.[15,16] Chemical analysis of graphite fibers showed the presence of oxygen-containing functional groups on the surface of even untreated fibers (Table VIII), but the oxidized fibers, particularly the nitric acid treated materials, had a considerably higher oxygen content.

The following scheme has been proposed by Rivin[15] and by Boehm[16] as the route by which the surface oxidation of carbon occurs:
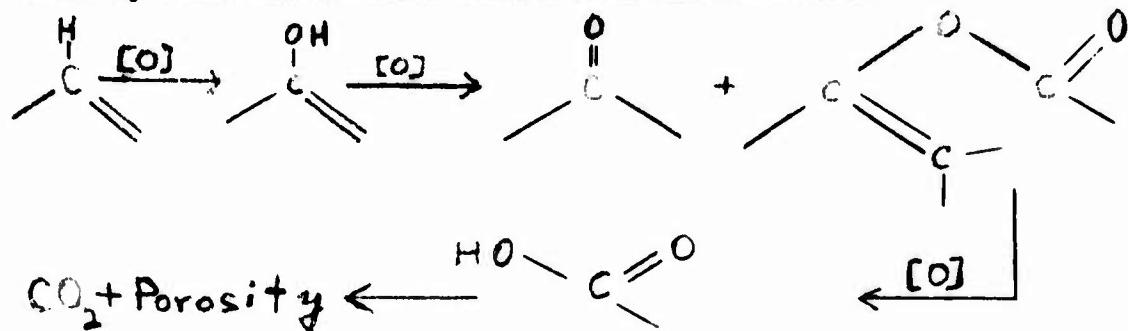
These carboxyl and phenolic hydroxyl functional groups on the carbon surface can act as "handles" to the resin by reacting with epoxy, amino or other chemical groups in the resin, thereby forming chemical bonds of high strength. Even if no chemical bonding is involved in the adhesive process, the higher oxygen content would alter the surface energy of the fiber and in this way change the adhesive properties.

In a particularly elegant experiment, Herrick[6] has produced strong evidence that the increase in surface chemical activity resulting from oxidation is more important than the surface area increase. Graphite fiber was oxidized with nitric acid to increase both the surface area and surface chemical activity. Hydrogen furnace reduction of the surface eliminated the chemical activity but had no effect on the surface area. Composites made from specimens treated in this way exhibited shear strengths near the level obtained by using untreated fibers. The logical conclusion was that chemical functionality was a logical more important influence than surface area in shear strength.

Oxygen containing surface groups affect the wetting properties of the surface. Untreated fiber is hydrophobic; oxidized fiber is hydrophilic and is more readily wet out by resin. Duffy has measured a critical surface tension, γ_c, of 46 dynes per centimeter for untreated graphite fiber.[21] This value of γ_c is very close to the measured value of 44 dynes per centimeter for the surface tension of uncured epoxy resins and would not be expected to lead to rapid wetting of fiber by resin. What effect oxidation of the fiber has on γ_c has not been determined (primarily because of the great uncertainty in using the normal contact angle measurements on such small filaments).[22,23] It would, however, be logical to expect the presence of oxygen groups on the surface to influence the surface energy. Observation of the wetting of oxidized yarn by epoxy resin showed that the treated yarn was much more readily wet out by the resin than the untreated material.

One other point should be made in this discussion. Some work has been reported on the effects of "heat cleaning" graphite yarn in order to improve the adhesion to resins.[10,24] In most cases the yarn was heated to a temperature of around 1100°C by its electrical resistance as it passed over energized pulleys. The heating was carried out in an inert atmosphere, either nitrogen or argon, and the fiber was coated with a polymer or impregnated with resin before it was reexposed to the atmosphere.

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The rationale for this treatment has apparently been that adsorbed gases, water and other impurities contaminate the fiber surface, lowering its critical surface tension and impeding wetting by resins. This is perfectly valid reasoning. Indeed, it was found that substantial shear strength increases resulted from such fiber treatment.

What seems to not have been given sufficient consideration is that the treatment conditions were not in actuality rigorous enough to exclude the possibility of fiber oxidation occurring. In most cases, the inert gas contained enough oxygen to result in some attack on the fiber. Even if oxygen is not present in the atmosphere, carbon at temperatures above $900°C$ is such a powerful reducing agent that adsorbed water, PVA, CO_2, etc. are all oxidizing agents toward it. Thus, it is quite probable that the effects attributed to the heat treatment are really a result of fiber oxidation, though the heat cleaning process, perhaps, aids the adhesion to resins.

CONCLUSIONS AND RECOMMENDATIONS

Fiber oxidation improves the shear strength of graphite fiber-epoxy composites.

The reasons for the improvement are complex and not fully understood. Both surface morphology and surface chemical activity are affected by oxidation; both of these influence adhesion to resins.

Fiber oxidation has great potential as a practical commercial treatment to increase the shear strength of graphite fiber composites. Process development work should emphasize continuous processing techniques for yarn.

A great deal more needs to be learned about the graphite fiber surface. The surface chemistry of the fiber should be examined in depth, and research should be carried out to determine the specific effects of fiber oxidation on the surface chemistry.

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TABLE I

SHEAR STRENGTHS OF UNIDIRECTIONAL FIBER-EPOXY COMPOSITES

FIBER	NOMINAL MODULUS[a]		COMPOSITE SHEAR STRENGTH[b,c]	
	psi	N/M^2	psi	N/M^2
VYB Roving	6×10^6	41×10^9	13,500	93.0×10^6
Pluton H-31	6×10^6	41×10^9	9,400	64.7×10^6
Thornel 25	25×10^6	172×10^9	3,600	24.8×10^6
Thornel 40	40×10^6	276×10^9	3,400	23.4×10^6
Thornel 50	50×10^6	345×10^9	3,800	26.2×10^6
RAE	68×10^6	468×10^9	2,900	20.0×10^6
Morganite I[d]	54×10^6	372×10^9	2,900	20.0×10^6
Morganite II[d]	38×10^6	262×10^9	7,200	49.6×10^6
HITCO HMG	25×10^6	172×10^9	6,350	43.7×10^6
Samco 320	38×10^6	262×10^9	2,630	18.1×10^6
S Glass	12.5×10^6	86×10^9	15,000	103.4×10^6
Boron Filament	60×10^6	414×10^9	14,000[e]	96.5×10^6
Silicon Carbide	60×10^6	414×10^9	11,000[f]	75.8×10^6

a. Manufacturer's data.
b. Short Beam Test, ASTM.
c. All NOL data unless otherwise noted.
d. Courtalds' materials are almost identical.
e. See reference 1.
f. See reference 1.

TABLE II

STRAND TENSILE TESTS OF OXIDIZED FIBERS

FIBER	TREATMENT	AVERAGE ULTIMATE TENSILE STR.		PERCENT DECREASE
		psi	N/M^2	
Thornel 25	None	198,000	13.7 X 10^8	-
	Nitric Acid	194,000	13.4 X 10^8	2
	Air Oxidation (400°C)	141,000	9.7 X 10^8	29
	RF Oxygen Plasma	180,000	12.4 X 10^8	9
	Sodium Hypochlorite	145,000	10.0 X 10^8	27
Thornel 40	None	193,000	13.3 X 10^8	-
	Nitric Acid	181,000	12.5 X 10^8	6
	Sodium Hypochlorite	168,000	11.6 X 10^8	13
	Air Oxidation	148,000	10.2 X 10^8	23
	RF Oxygen Plasma	170,000	11.7 X 10^8	12

TABLE III

EFFECT OF FIBER OXIDATION ON THORNEL 50 COMPOSITE PROPERTIES
(Resin System: ERL 2256/ZZL 0820 (27 phr))

FIBER TREATMENT	COMPOSITE PROPERTIES				STRAND TENSILE STRENGTH	
	DENSITY g/cc	FIBER Vol.,%	SHEAR psi	STRENGTH N/M^2	psi	N/M^2
None (PVA Finish)	1.43	58	3660	25.2×10^6	288,000	19.9×10^8
Water Wash	1.45	61	3820	26.3×10^6	220,000	15.2×10^8
Nitric Acid	1.46	57	5850	40.3×10^6	220,000	15.2×10^8
Sodium Hypochlorite	1.41	-	4330	29.9×10^6	123,000	8.5×10^8
Chromic Acid	1.59	59	3510	24.2×10^6	190,000	13.1×10^8
Brodie's Reagent ($KClO_3 + HNO_3$)	1.45	57	4080	28.1×10^6	138,000	9.5×10^8
Air (400°C)	1.44	57	3790	26.1×10^6	178,000	12.3×10^8

TABLE IV

EFFECT OF 24-HOUR NITRIC ACID FIBER TREATMENT
ON COMPOSITE SHEAR STRENGTH

	SHORT BEAM SHEAR STRENGTH*			
	UNTREATED		TREATED	
FIBER	psi	N/M²	psi	N/M²
HMG 25	3200	22.1×10^6	3400	23.4×10^6
MORGANITE I	2900	20.0×10^6	9600	66.2×10^6
SAMCO 320	3400	23.4×10^6	5000	34.5×10^6

* Resin system ERLA 02256/ZZL 0820, span-to-depth ratio 5:1.

TABLE V

EFFECT OF SIX-HOUR BOIL ON SHEAR STRENGTH OF NOL RINGS
MADE FROM OXIDIZED THORNEL 25 YARN*

	AVERAGE SHEAR STRENGTH, SHORT BEAM SPECIMEN			
	Dry		6-Hour Boil	
FIBER TREATMENT	psi	N/M²	psi	N/M²
Untreated (PVA, Coating)	3600	24.8 x 10⁶	3500	24.1 x 10⁶
Untreated (no PVA coating)	4100	28.3 x 10⁶	4100	28.3 x 10⁶
Nitric Acid Oxidized	7200	49.6 x 10⁶	6600	45.5 x 10⁶
Air Oxidized (400°C)	5900	40.7 x 10⁶	6400	44.1 x 10⁶
Oxidized in RF Discharge	5800	40.0 x 10⁶	6200	42.8 x 10⁶
Sodium Hypochlorite Oxidized	5400	37.2 x 10⁶	5600	38.6 x 10⁶
Oxidized in Ozone	5000	34.5 x 10⁶	4800	33.1 x 10⁶

* Resin System: ERLA 2256/ZZL 0820 (27 phr); vacuum impregnated.

TABLE V

EFFECT OF SIX-HOUR BOIL ON SHEAR STRENGTH OF NOL RINGS
MADE FROM OXIDIZED THORNEL 25 YARN*

	AVERAGE SHEAR STRENGTH, SHORT BEAM SPECIMEN			
	Dry		6-Hour Boil	
FIBER TREATMENT	psi	N/M^2	psi	N/M^2
Untreated (PVA, Coating)	3600	24.8×10^6	3500	24.1×10^6
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Nitric Acid Oxidized	7200	49.6×10^6	6600	45.5×10^6
Air Oxidized (400°C)	5900	40.7×10^6	6400	44.1×10^6
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Oxidized in Ozone	5000	34.5×10^6	4800	33.1×10^6

* Resin System: ERLA 2256/ZZL 0820 (27 phr); vacuum impregnated.

TABLE VI

EFFECT OF 24-HOUR NITRIC ACID
OXIDATION ON FIBER WEIGHT

FIBER	WEIGHT LOSS (%)
Thornel 25	1.4
Thornel 40	1.6
Thornel 50*	0.9*
Morganite I	0.9
Hitco HMG	3.5
Samco 320	0.8

* Corrected for 0.9% weight loss caused by removal
  of PVA coating.

TABLE VII

EFFECT OF FIBER OXIDATION ON SURFACE AREA

Thornel 40 Fibers

Treatment	BET Surface Area (M^2/gm)
"Water Finish" (no treatment)	0.8
Nitric Acid Oxidation	11.3
Air Oxidation (400°C)	1.4
Oxidation in RF Plasma	1.3

TABLE VIII

CHEMICAL ANALYSIS OF SURFACE GROUPS ON OXIDIZED GRAPHITE FIBER

SPECIMEN	CHEMICAL ANALYSIS[a], PERCENTAGE OF			
	ACTIVE HYDROGEN	CARBOXYL	PHENOLIC HYDROXYL	TOTAL OXYGEN (COMBUSTION)
Unoxidized Thornel	0.01	0.11	0.13	0.1
Nitric Acid Oxidized Thornel 40	0.04	1.0	0.5	1.9
Air Oxidized (400°C) Thornel 40	0.03	--	0.4	0.3

a. See reference 15.

1a   1b

FIG. 1 SCANNING ELECTRON PHOTOMICROGRAPHS OF GRAPHITE FIBER SURFACES
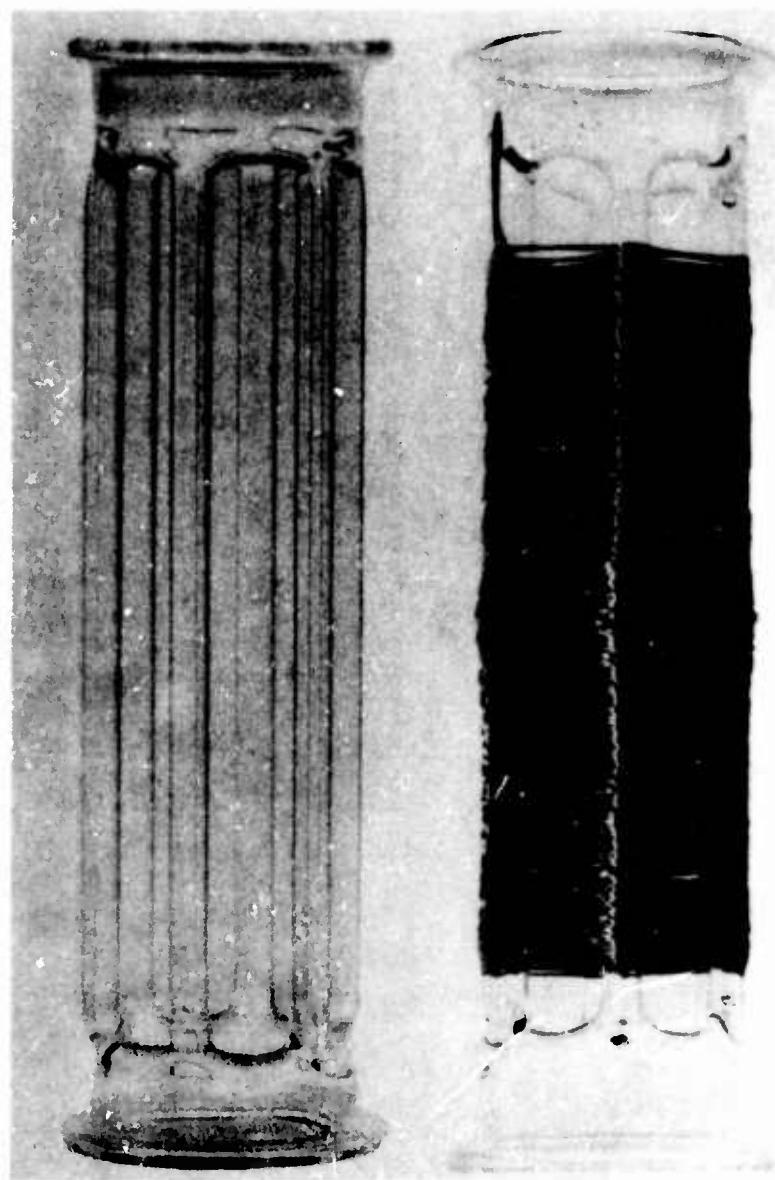
FIG. 2 SPOOL FOR SOLUTION TREATMENTS OF GRAPHITE YARN
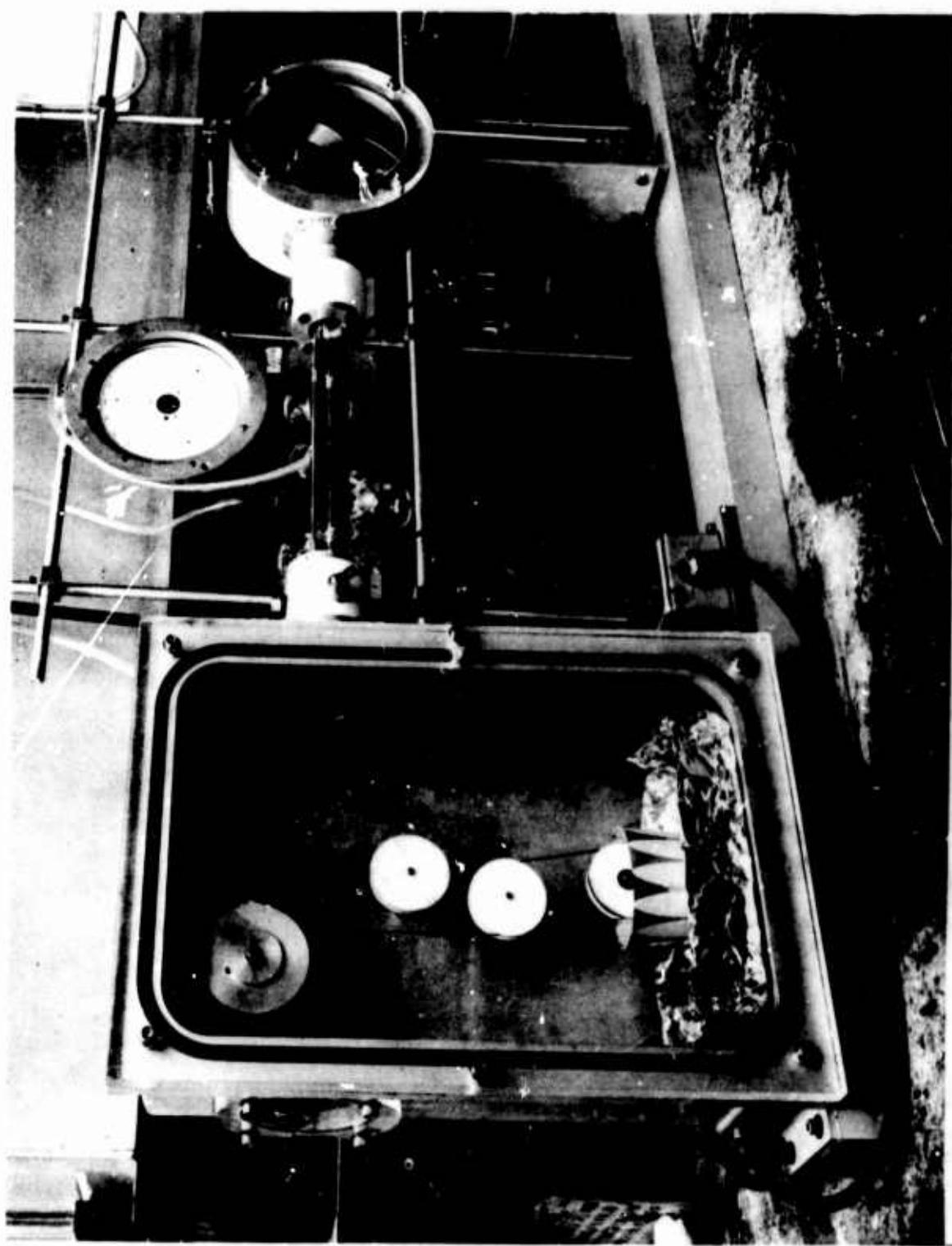
FIG. 3 APPARATUS FOR CONTINUOUS OXIDATION OF GRAPHITE YARN
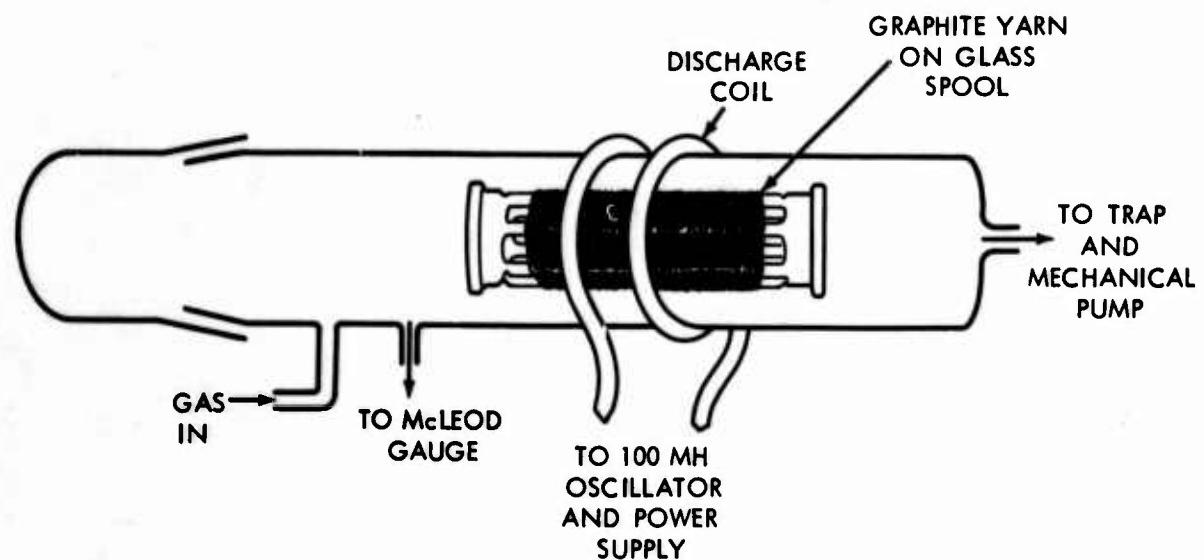
FIG. 4 APPARATUS FOR RF PLASMA OXIDATION OF
GRAPHITE YARN
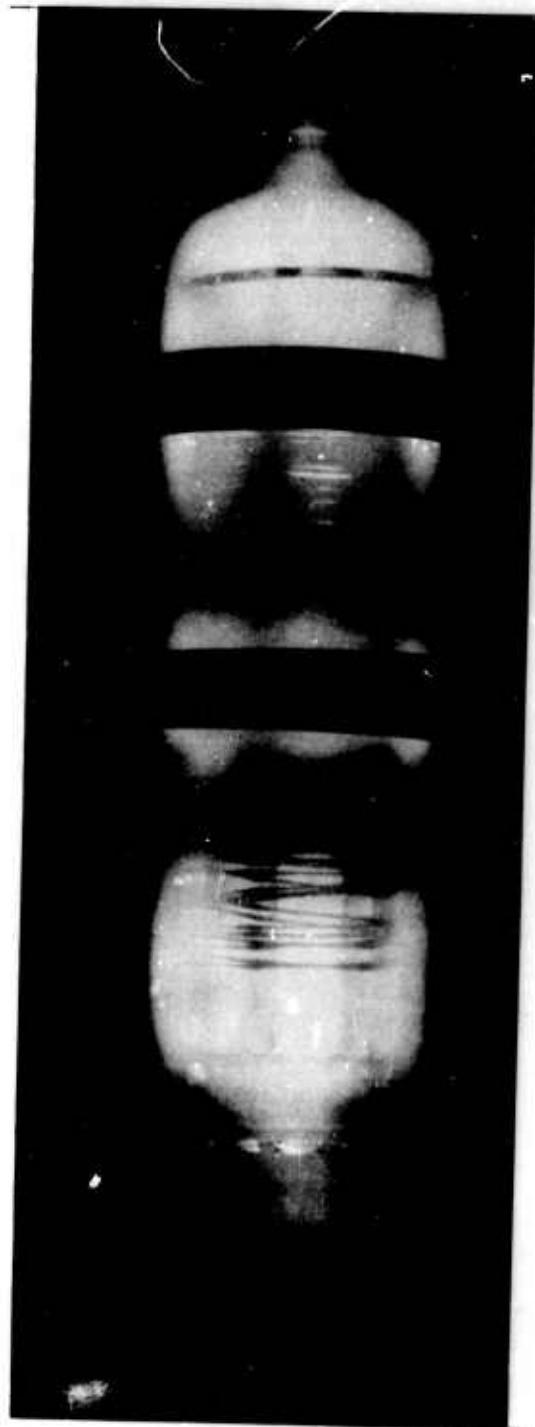
FIG. 5 OXIDATION OF GRAPHITE YARN IN "COLD PLASMA" R.F. DISCHARGE
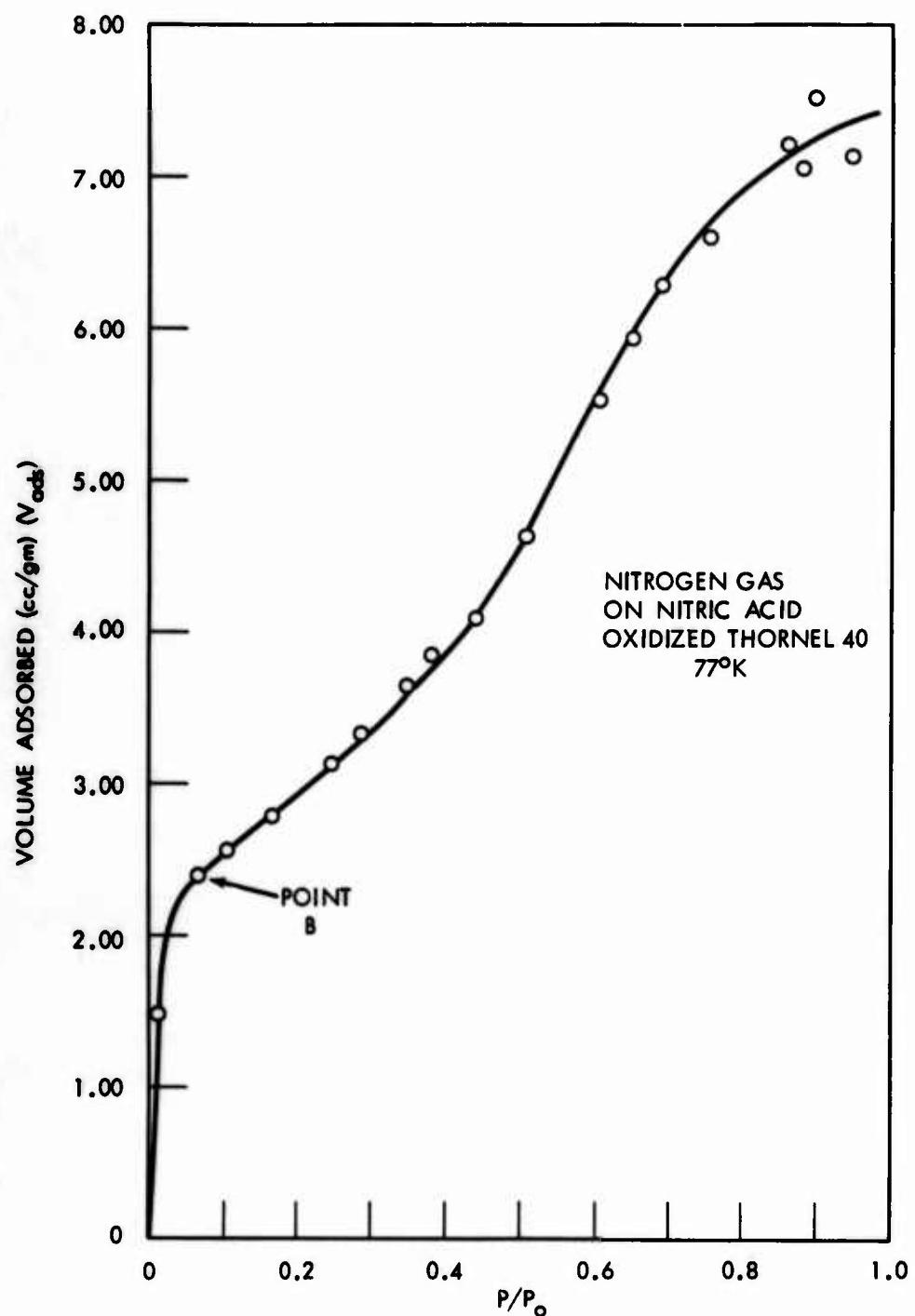
FIG. 6 ADSORPTION ISOTHERM
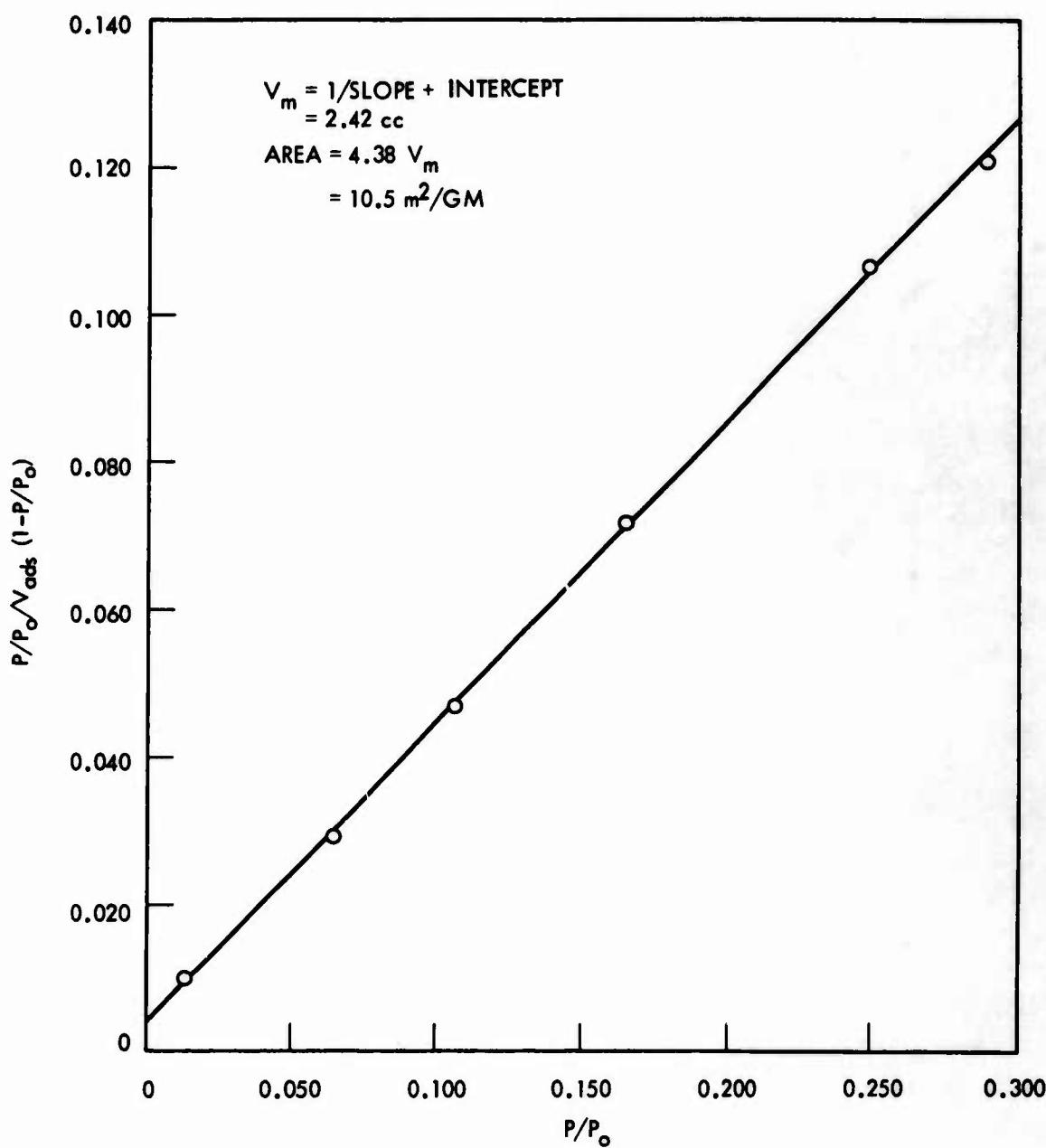
FIG. 7 BET PLOT FOR NITRIC ACID OXIDIZED THORNEL 40

RESIN SYSTEM: ERLA 2256/ZZL0820 (27 PHR); VACUUM IMPREGNATED

AVERAGE SHEAR STRENGTH, SHORT BEAM TEST (PSI)

FIBER TREATMENT

PVA FINISH

WATER FINISH

NITRIC ACID OXIDIZED

AIR OXIDIZED (400°)

OXIDIZED IN RF DISCHARGE

SODIUM HYPOCHLORITE

OZONE

($\times 10^2$)
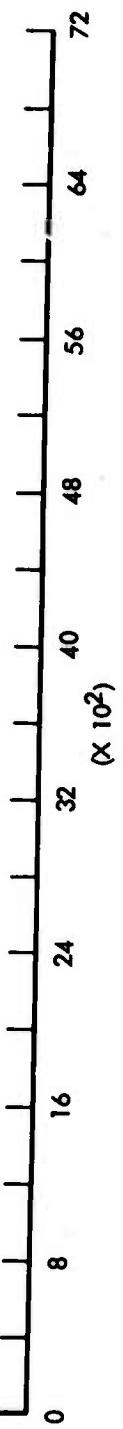
FIG. 8 EFFECT OF OXIDATION ON SHEAR STRENGTH OF THORNEL 25 NOL RINGS
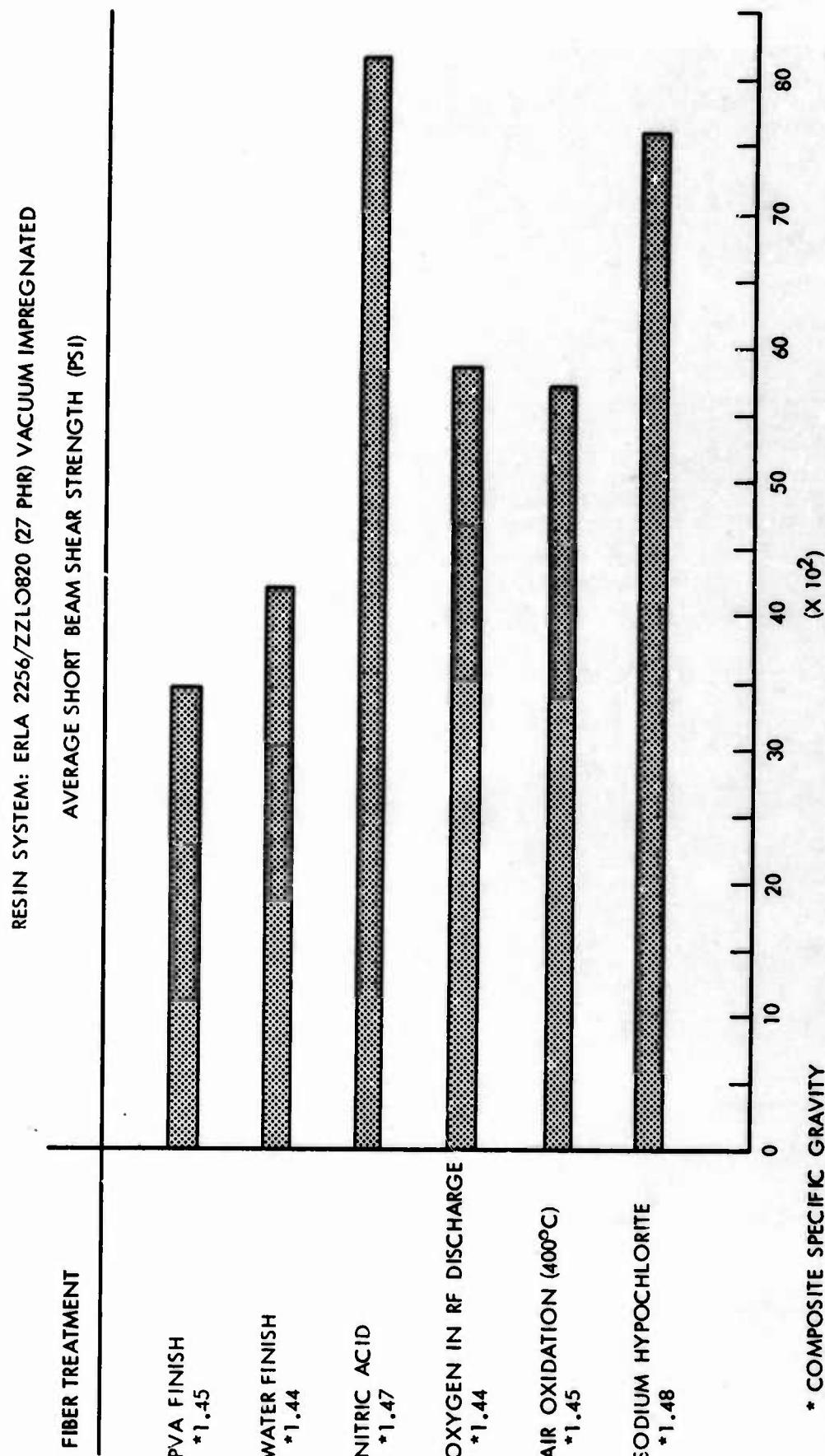
FIG. 9 EFFECT OF OXIDATION ON SHEAR STRENGTH OF THORNEL 40 NOL RINGS

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13. ABSTRACT

In order to improve the low interlaminar shear strengths which hinder widespread use of epoxy composites made from high modulus graphite fibers, an investigation was made of fiber surface treatments. Treatments of the fibers with various oxidizing systems was found to increase composite interlaminar shear strengths as much as twofold. Among the oxidizing agents studied, concentrated nitric acid was the most effective in increasing fiber-resin adhesion without significantly decreasing fiber strength. Exposure of the fiber to low pressure oxygen in the presence of an R. F. plasma was also an effective treatment.

The mechanism by which fiber oxidation improves composite shear strength appears to be related both to an increase in fiber surface area and to an alteration of the nature of the surface resulting from the attachment of oxygen-containing functional groups.

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14 KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
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Graphite Fibers						
Graphite Composites						
Surface Treatments						
Finishes						